



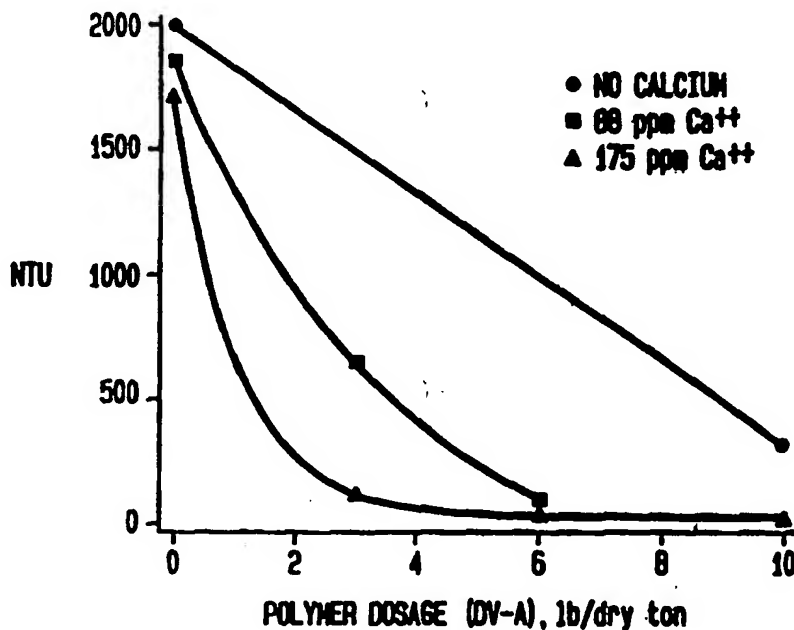
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(71) Applicant: RHODIA INC. [US/US]; 259 Prospect Plains Road, Cranbury, NJ 08512-7500 (US).			
(72) Inventor: LARSON, Eric, Heath; 132 Derby Drive, Freehold, NJ 07728 (US).		Published With international search report.	
(74) Agents: SHEDDEN, John, A. et al.; Rhodia Inc., 259 Prospect Plains Road, Cranbury, NJ 08512-7500 (US).			

(54) Title: PROCESS FOR REMOVING WATERBORNE FLEXOGRAPHIC INKS FROM SUBSTRATES

## (57) Abstract

A process for removing waterborne flexographic inks from paper stock comprising the steps of: (a) forming a slurry by pulping paper containing waterborne flexographic inks in an aqueous medium having a pH of greater than 6 which includes: (1) one or more pH adjusting agents; (2) one or more nonionic surfactants; and (3) one or more anionic polyelectrolytes; and (b) subjecting the slurry produced in step (a) to a flotation cell including one or more cationic polymers is provided. The flotation cell can include one or more sources of calcium (2+) ions, magnesium (2+) ions, aluminum (2+) ions or aluminum (3+) ions. Examples of sources of materials which may be selected include the following materials: calcium chloride, aluminum chloride, magnesium chloride, calcium sulfate, magnesium sulfate or aluminum sulfate. In practice, when present, the source of positive ions is present in the flotation cell in amounts ranging from about 10 to about 1000 ppm, more preferably between about 300 and about 500 ppm.



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## PROCESS FOR REMOVING WATERBORNE FLEXOGRAPHIC INKS FROM SUBSTRATES

### Background of the Invention

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#### 1. Field of the Invention

The present invention relates to a process for removing waterborne flexographic printing inks from substrates containing them. More particularly, the invention comprises removing  
10 waterborne (hydrophilic inks) from a substrate by using pulping and a flotation deinking process wherein the aqueous mediums have a neutral or basic pH, and include a nonionic surfactant and an anionic polyelectrolyte and wherein the flotation cell includes one or more cationic polymers, and, optionally, either calcium, magnesium or aluminum ions and a foam reducing surface active component.

15

#### 2. Technology Description

Water borne inks used to print newspapers by flexographic processes offer reduced emissions of volatile organic compounds to the environment during the printing process  
20 compared to oil based ink formulations. These inks, however, interfere with the recycling of the same newspapers as the colloidal nature of the pigments used combined with their hydrophilic nature make their separation from paper fiber difficult. The use of these inks can be viewed as an exchange of one type of environmental liability for another.

25 Water-borne or hydrophilic inks are characterized as having water as the vehicle or major liquid component in which is dissolved or suspended the large number of additives used by the ink formulator to provide a variety of desirable properties required for application on the printing press. These additives may include pigments and dyes (e.g., carbon black), for coloring the printed surface, binders such as dissolved or suspended  
30 polymers (e.g., polyacrylate), thickeners to control the rheology of the ink, water miscible solvents such as alcohols to control drying rate, surface tension, settling stability and other properties. In addition surfactants to control a variety of surface properties and control or minimize foaming, and dispersants to maintain product quality in storage and use are common. Buffers and other pH modifiers are commonly used. One common  
35 class of waterborne inks contains a carboxylated polymer and a fugitive base such as

ammonia hydroxide which is selected to provide a medium that the resin is soluble. The carboxylated polymer is soluble in the aqueous vehicle at high pH; when the ink is applied to paper on the printing press, the base vaporizes reducing the pH. This results in desolubilization of the polymer which improves the attachment of pigment to the substrate.

The impact of using waterborne inks on conventional deinking processes is severe; inclusion of as little as 5% flexographic news into a newsprint recycle furnish can significantly reduce the brightness of the recycled pulp.

Conventional practice has been to process flexographic newsprint using wash deinking processes. While wash deinking is easy to operate, and requires minimal capital investment, the large volumes of water required make wash deinking an increasingly environmentally unacceptable practice. The paper industry as a whole is under severe pressure to reduce rates of water consumption. As a result the trend in the recycled paper industry is towards use of flotation or hybrid flotation/wash systems for ink removal. Flotation is particularly ill-suited for removal of water borne ink from recycle newsprint as both the small particle size and hydrophilic nature of the ink result in poor rates of bubble attachment and low separation efficiencies. The poor effectiveness of flotation in removal of water borne inks is a particular obstacle to recycling newsprint so contaminated, and in some cases restricts the acceptance of the use of water borne inks as a means to reduce emissions of volatile organic compounds.

There have been proposals describing a two stage process to remove water borne pigments using a flotation step under acidic conditions followed by a flotation step under alkaline conditions. Maintenance of acid conditions limits the hydrophilicity of the pigment particles, and reduces the degree of dispersion of such inks. The benefit of this procedure is avoidance of the high water consumption of a wash system, however the capital and operating costs of this process are greater than that of a single flotation stage process, and in addition pulping under acidic conditions is difficult if the waste paper contains alkaline fillers such as calcium carbonate.

Printers and converters facing increasingly stringent air quality regulations have turned to use of water based inks as a means of avoiding capital expenditures for emissions control systems. The use of these water based inks in flexographic news printing has

been a severe challenge for the paper recycler. Under alkaline deinking conditions the pigments used in these inks disperse forming submicron particles with hydrophilic surfaces. Zeta potential measurements show that these pigments are highly anionic. While studies have shown that calcium soap deinking systems can float flexographic pigments in the absence of fiber, separation by flotation using calcium soap systems in the presence of fiber is not effective.

Water based gravure inks possess similar characteristics. The recycling of water contaminated with finely divided, highly anionic pigment can overload clarifiers. This results in delivery of poor quality water to other deink mill unit operations, leading finally to unacceptable process performance

A variety of approaches to recycling wastepaper printed with water based pigments have been proposed. One has been the development of alternatives to the acrylate binders and dispersants now used in water dispersible ink. Addition of organoclays as collectors has been tested. Cationic polymers have been the subject of considerable interest, although most evaluations have been with limited flexographic news contents. Pulping at low pH followed by a low pH flotation shows benefits due to reduced dispersion of the hydrophilic pigments, however this must be followed by a high pH deinking cycle for oil based ink removal. Use of washing for pigment removal followed by membrane separation for water recovery has also been proposed.

Strategies for recycling flexographic news in conventional deinking systems include limiting the percentage in the furnish to less than 5-10%, or using flexographic based furnishes on an intermittent basis, allowing water recycle cleanup unit operations to catch up during periods of time when non-flexographic based materials are deinked. Recyclers have found that during periods of tight wastepaper supply grade deterioration leads to more limited ability to process water based pigment sources. It is precisely during these periods of tight supply the ability to process a wide variety of wastepapers would be the most valuable.

Despite the above teachings, there still exists a need in the art for a process for removing hydrophilic inks under alkaline conditions by using a flotation method as such a method provides an environmentally friendly, cost effective way to remove such hydrophilic inks.

Brief Summary of the Invention

5 In accordance with the present invention a novel process for deinking is provided which reveals a surprising combination of beneficial effects under the conditions of alkaline flotation deinking of newspaper printed with water borne ink in the presence of nonionic surfactants and dispersants during pulping and in the presence of cationic polymers during flotation. The novel process provides an environmentally friendly, cost effective way to remove hydrophilic inks from substrate.

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One embodiment of the present invention provides A process for removing water borne flexographic inks from paper stock comprising the steps of:

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(a) forming a slurry by pulping paper containing water borne flexographic inks in an aqueous medium having a pH of greater than 6 which includes:

- (1) one or more pH adjusting agents;
- (2) one or more nonionic surfactants; and
- (3) one or more anionic polyelectrolytes; and

20

(b) subjecting the slurry produced in step (a) to a flotation cell including one or more cationic polymers.

25

In particularly preferred embodiments, the pH of step (a) is between 8.0 and about 10.5, the nonionic surfactant present in step (a) is an alkoxyated fatty acid, the anionic polyelectrolyte present in both step (a) is a copolymer of maleic anhydride and isobutylene. In even more preferred embodiments, the flotation cell further includes one or more defoaming agents and one or more sources of calcium ions.

30

Another embodiment of the present invention comprises a process for removing flexographic inks from substrates comprising the steps of:

(a) pulping said substrates to form a slurry; and

(b) subjecting said slurry to a flotation cell including one or more cationic polymers, a source of calcium, magnesium or aluminum ions and a defoaming agent.

5 An object of the present invention is to provide a process which is effective in removing hydrophilic flexographic inks from a substrate which uses flotation processing.

Still another object of the present invention is to provide a process which is effective in removing hydrophilic flexographic inks from a substrate, requires a minimal amount of water for use, and is cost effective.

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These, and other objects, will readily be apparent to those skilled in the art as reference is made to the drawings and to the detailed description of the preferred embodiment.

#### Brief Description of the Drawings

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Tables 1 and 2 show results from Example 1.

Tables 3 and 4 are the additives into the pulper and flotation cell, respectively, for Example 2.

20 Figure 1 shows results from Example 1.

Figures 2-12 show results from Example 2.

#### Detailed Description of the Preferred Embodiment

25

In describing the preferred embodiment, certain terminology will be utilized for the sake of clarity. Such terminology is intended to encompass the recited embodiment, as well as all technical equivalents which operate in a similar manner for a similar purpose to achieve a similar result.

30

The present invention provides a novel process for removing water borne or hydrophilic inks from paper stock while using flotation processing.

35 The first step of the invention is directed to pulping paper containing water borne flexographic inks in an aqueous medium having a pH of greater than 6 which includes:

- (1) one or more pH adjusting agents;
- (2) one or more nonionic surfactants; and
- (3) one or more anionic polyelectrolytes.

5

The paper to be pulped, which also includes by definition any cellulosic sheet materials containing hydrophilic flexographic inks including, for example, newspaper, filled and unfilled papers and paper boards is provided to a pulper at alkaline pH conditions. The ink present on the paper to be pulped comprises water-borne flexographic ink. This type of ink, as discussed above, differs from letterpress and offset ink by having water as the liquid vehicle used to apply the pigment to the substrate. In practice, the water amount of the ink generally ranges from about 50 to about 90 percent by weight of the entire ink, with amounts between about 65 and about 77 percent by weight of the ink being commonly used in industry. Until the present invention, these types of inks have been extremely difficult to effectively remove from a paper substrate as they tend to form small particles during the pulping step which are difficult to disperse into the pulping aqueous medium.

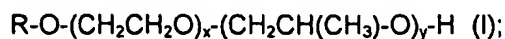
The pH of the aqueous medium of the pulper is maintained between about 6 to about 10.5, more preferably between about 8 to about 10, and most preferably between about 9 to about 9.5. Maintenance of the pH is accomplished by adding one or more pH adjusting agents to the pulper. Agents which may be selected include any of those commonly known in the art which are capable of adjusting the pH to between 6.0 and about 10.5. Examples of such agents include, but are not limited to the following materials: of NaOH, NH<sub>4</sub>OH, KOH, Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, HCl, CH<sub>3</sub>COOH and mixtures thereof. The amount of pH adjusting agent added to the pulper is that which is required to obtain the desired pH. This amount can be readily measured by those skilled in the art.

Also present in the aqueous medium of the pulper is one or more nonionic surfactants. The surfactant functions to disperse the ink into the aqueous medium during pulping. Nonionic surfactants suitable for use are higher (greater than C<sub>8</sub>) aliphatic alcohol alkoxylates, aliphatic acid alkoxylates, higher aromatic alcohol alkoxylates, fatty acid amides of alkanolamines, fatty acid amide alkoxylates, propylene glycol alkoxylates, block or random copolymers of ethylene and propylene oxide, higher (greater than C<sub>8</sub>) alcohol polyethylene polypropylene block or random adducts and mixtures thereof. Specific



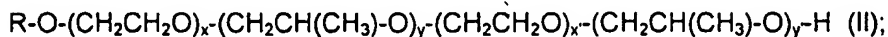
examples of surfactants which may be used in accordance with the present invention include the following classes of chemicals:

- 1) a fatty alcohol having a carbon number of from about 8 to about 22,  
5 alkoxyated with ethylene oxide and propylene oxide, as represented by formula (I)



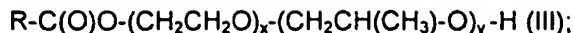
10 wherein R is a straight-chain or branched alkyl group having a carbon number of from about 8 to about 22; x represents the number of oxyethylene groups per molecule and is in the range of from about 3 to about 25; and y represents the number of oxypropylene groups per molecule and is in the range of from about 1 to about 10. Examples of commercially  
15 available products are sold under the InkMaster<sup>®</sup> and Antarox<sup>®</sup> trademarks by Rhône-Poulenc Inc.;

- 2) a fatty alcohol having a carbon number of from about 8 to about 22,  
20 alkoxyated with ethylene oxide and propylene oxide, as represented by formula (II):



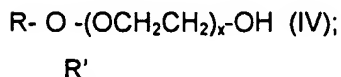
25 wherein R is a straight-chain or branched alkyl group having a carbon number of from about 8 to about 22; x and x', which may be the same or different, represents the number of oxyethylene groups per molecule and is in the range of from about 2 to about 25; and y and y', which may be the same or different represents the number of oxypropylene groups per  
30 molecule and is in the range of from 0 to about 10. Examples of commercially available products are sold under the InkMaster<sup>®</sup> trademark by Rhône-Poulenc Inc.;

- 3) a fatty acid having a carbon number of from about 8 to about 22,  
35 alkoxyated with ethylene oxide and propylene oxide, as represented by formula (III):



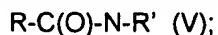
5 wherein R is a straight-chain or branched alkyl group having a carbon number of from about 8 to about 22; x represents the number of oxyethylene groups per molecule and is in the range of from about 3 to about 25; and y represents the number of oxypropylene groups per molecule and is in the range of from about 2 to about 15. Examples of commercially available products are Lionsurf<sup>®</sup>, Nonatell<sup>®</sup>, Hipochem<sup>®</sup>, and Berocell<sup>®</sup> products sold respectively by Lion Industries, Inc., Shell Oil Company, High Point Chemical Corp. and EKA Nobel AB;

10 4) an aromatic alcohol such as phenol having alkyl chain(s) with a carbon number of from about 8 to about 20, alkoxylated with ethylene oxide, as represented by formula (IV):



20 wherein R and R' independently are H or an alkyl group which is branched or straight-chain having a carbon number of from about 8 to about 14; and x is the number of oxyethylene groups per molecule and is in the range of from about 1 to about 20. Examples of commercially available products are InkMaster<sup>®</sup>, Igepal<sup>®</sup>, and Alkasurf<sup>®</sup>, products sold by Rhône-Poulenc Inc.;

25 5) fatty amide of alkanolamide of formula (V):

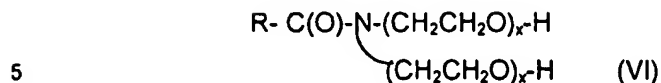


30

R''

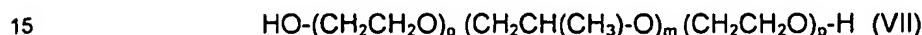
wherein R' and R'' may be the same or different and are H or CH<sub>2</sub>CH<sub>2</sub>OH or CH<sub>2</sub>CH(CH<sub>3</sub>)-OH and R is a fatty alkyl group having a carbon number of from about 8 to about 20. Examples of commercially available products are Alkamide<sup>®</sup> products sold by Rhône-Poulenc Inc.;

- 6) an alkoxyated fatty acid amide of alkanolamide of formula (VI):



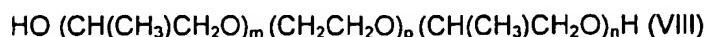
wherein R is a fatty alkyl group having a carbon number of from about 8 to about 20; and x represents the number of oxyethylene groups per molecule and is in the range of from about 2 to about 10. Examples of commercially available products are Alkamide<sup>®</sup> products sold by Rhône-Poulenc Inc.;

- 7) a propylene glycol alkoxyate of formula (VII):



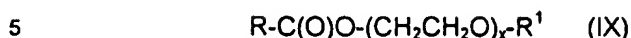
wherein o and p are the number of oxyethylene groups per molecule and are in the range of from about 3 to about 15 and m is the number of oxypropylene groups per molecule and is in the range of from about 25 to about 40. Examples of commercially available products are Antarox<sup>®</sup> products sold by Rhône-Poulenc Inc. and products having a CTFA designation of Poloxamer;

- 8) a block or random copolymer of ethylene and propylene oxide of formula (VIII):



wherein m and n are the number of oxypropylene groups per molecule and are in the range of from about 10 to about 25 and p is the number of oxyethylene groups per molecule and is in the range of from about 5 to about 25. Examples of commercially available products are Antarox<sup>®</sup> products sold by Rhône-Poulenc Inc. and products having a CTFA designation of Merxopol;

- 9) an ethoxylated fatty acid glycol and/or polyethylene glycol esters of formula (IX):



wherein R is a fatty alcohol of greater than C<sub>8</sub>; R<sup>1</sup> is alkyl of greater than C<sub>8</sub> or H; and x represents the number of oxyethylene groups per molecule and is in the range of from about 5 to about 200. Examples of  
10 commercially available products are Alkamus<sup>®</sup> products sold by Rhône-Poulenc Inc. and products having a PEG castor oil CTFA designation; and

- 10) an ethoxylated fatty alcohol of formula (X):



wherein R is a fatty alcohol; and x represents the number of oxyethylene groups per molecule and is in the range of from about 1 to about 20  
20 Examples of commercially available products are Rhodasurf<sup>®</sup> products sold by Rhône-Poulenc Inc.

More preferred nonionic surfactants within the above classes include:

- 25 1) Those of Formula (I) wherein R is a straight-chain or branched alkyl group having a carbon number of from about 16 to 20, x represents the number of oxyethylene groups per molecule and is in the range of from about 10 to about 20, and y represents the number of oxypropylene groups per molecule and is in the range of from about 4 to about 8. A commercial  
30 example of such a nonionic surfactant is InkMaster<sup>®</sup> 750; or wherein R is a straight-chain or branched alkyl group having a carbon number of from about 8 to 14, x represents the number of oxyethylene groups per molecule and is in the range of from about 3 to about 12, and y represents the number of oxypropylene groups per molecule and is in the

range of from about 1 to about 6. A commercial example of such a nonionic surfactant is Antarox® LA-EP-16, sold by Rhône-Poulenc;

- 5           2)   Those of Formula (II) wherein R is a straight-chain or branched alkyl group having a carbon number of from about 16 to about 20, x and x' represents the number of oxyethylene groups per molecule and is in the range of from about 4 to about 10, and y and y' represents the number of oxypropylene groups per molecule and is in the range of from about 1 to about 5;
- 10           3)   Those of Formula (III) wherein R is a straight-chain or branched alkyl group having a carbon number of from about 12 to about 18, x represents the number of oxyethylene groups per molecule and is in the range of from about 3 to about 25, and y represents the number of oxypropylene groups per molecule and is in the range of from about 2 to about 15. A commercial example of such a nonionic surfactant is Hipochem® DI600, sold by High Point Chemicals;
- 15           4)   Those of Formula (IV) wherein R and R' is H or a branched or straight-chain having a carbon number of from about 8 to about 14 and x is the number of oxyethylene groups per molecule and is in the range of from about 8 to about 12. A commercial example of such a nonionic surfactant is InkMaster®730;
- 20           5)   Those of Formula (V) wherein R' and R'' are H or CH<sub>2</sub>CH<sub>2</sub>OH or CH<sub>2</sub>CH(CH<sub>3</sub>)-OH and R is a fatty alkyl group having a carbon number of from about 8 to about 14;
- 25           6)   Those of Formula (VI) wherein R is a fatty alkyl group having a carbon number of from about 8 to about 14 and x represents the number of oxyethylene groups per molecule and is in the range of from about 4 to about 8;
- 30           7)   Those of Formula (IX) wherein R is a fatty alcohol of greater than C<sub>8</sub>; R<sup>1</sup> is alkyl of greater than C<sub>8</sub> or H; and x represents the number of
- 35

oxyethylene groups per molecule and is in the range of from about 8 to about 30; and

- 5           8) Those of Formula (X) wherein R is a fatty alcohol having a carbon number from about 12 to about 18, and x represents the number of oxyethylene groups per molecule and is in the range of from about 5 to about 15. A commercial example of such a nonionic surfactant is Rhodasurf® BC720, sold by Rhône-Poulenc Inc.;

- 10       Of the above, the use of the following classes of nonionic surfactants is particularly suggested: those of Formula (I), (II), (IX) as defined above.

15       The amount of surfactant present in the aqueous medium of the pulper ranges from about 0.05 to about 3.0 percent by weight based upon the dry weight of all paper added to the pulper, with amounts ranging from about 0.1 to about 0.5 percent being more preferred and amounts ranging from about 0.2 to about 0.4 percent being even more preferred

20       Also present in the aqueous medium of the pulper is one or more anionic polyelectrolytes. Such materials are characterized by being anionic in nature and function to reduce redeposition of the carbon black pigment to the pulp fibers.

25       Polyelectrolytes found to be particularly effective in this application include the copolymers of maleic anhydride and isobutylene, preferably those having a molecular weight of about 40,000. Other anionic polyelectrolytes which are recommended include polyacrylic acid, preferably having a molecular weight of about 5,000, and the formaldehyde condensate of methylnaphthalene sulfonic acid, preferably having a molecular weight of about 300 to about 4,000.

30       Other anionic polyelectrolytes which may be selected include polymers containing 2-acrylamidopropane sulfonic acid, polysaccharides, polyesters, hydrolyzed polyacrylamides, methacrylic acid, itaconic acid, and similar vinylic compounds with anionic functional groups, as well as condensation polymers containing anionic functional groups, and naturally occurring polymers containing such functionality, either  
35       naturally, or through chemical modification. Choice of the most preferred product may

depend on local economic conditions and processing details that vary depending on specific applications.

5 The amount of anionic polyelectrolyte present in the aqueous medium is between about 0.01 to about 2.0 percent by weight of the dry weight of all paper stock in the pulper.

10 Optionally present in the aqueous medium of the pulper are commonly known deinking additives added in amounts recognized by those skilled in the art. Such additives include, but are not limited to bleaches, sodium silicate, coagulants, detergent builders, other detergents and the like. In addition, the pulper may also include an amount of newsprint printed with a hydrophobic ink. The amount of such newsprint may range from about 10 to about 90 percent by weight of the total amount of paper added, more preferably between about 10 and about 50 percent.

15 In preferred embodiments, also present during the pulping step is an amount of paper which is different from that being processed and contains inorganic fillers, coatings or mixtures thereof. Particularly preferred is the use of coated magazine stock, or filled stock wherein the filler material is an inorganic material such as  $\text{CaCO}_3$ ,  $\text{TiO}_2$ , clay materials, and the like. The ink present on the coated or filled stock may be either  
20 hydrophobic or hydrophilic, the key criteria being that the added stock have a coating and/or inorganic filler material.

The amount of added coated and/or filled stock is between about 10 to about 50 percent by weight of all paper material added to the pulper. More preferred is the use of  
25 between about 10 to about 50 percent by weight of all paper material added to the pulper, and even most preferred is the use of between about 10 to about 50 percent by weight of all paper material added to the pulper.

It is important to maintain an appropriate pulp slurry temperature during pulping.  
30 Determining the appropriate temperature range is within the skill of an artisan. Generally the range is from about 40°C to about 65°C, more preferably from about 45°C to about 60°C.

The activation period is the time needed to allow substantially all of the paper fibers in  
35 the pulp slurry to come into contact with the aqueous medium. Conditions such as the

degree of dilution of the pulp slurry and the utilization of agitation can effect the amount of time needed. The determination of the appropriate amount of time needed is within the skill of an artisan. Generally, this time period can range from about 5 to about 90, preferably from about 10 to about 60 and most preferably from about 15 to about 30  
5 minutes.

Once the paper added to the pulper has been sufficiently slurried in the aqueous medium, the slurry is transferred to a flotation cell which is typically maintained at an alkaline pH and includes one or more cationic polymers.

10

The pH of the flotation cell is maintained between about 6 to about 10.5, more preferably between about 8.5 to about 9.5, and most preferably between about 9 to about 9.5. This pH often is the pH of the slurry which is provided to the flotation cell. If necessary to provide the desired pH profile, one or more of the pH adjusting agents which have been described in  
15 connection with the pulping step may be added in amounts to yield a pH in the flotation cell as defined above.

Also present in the flotation cell is one or more cationic polymers. Preferred cationic polymers which may be selected include any polymeric material which includes one or more  
20 cations, preferably cationic nitrogens.

Examples of such polymers are disclosed in copending U.S. Application Serial No. 08/573,710, filed on December 18, 1995. To the extent necessary for completion, this reference is hereby incorporated by reference.

25

In preferred embodiments, the polymer is a copolymer of :

(A) from about 0.1 - 99.5, more preferably from about 5-95, most preferably from about 20-95 weight percent based on total weight monomers of at least one vinyl  
30 monomer having at least one quaternized nitrogen atom;

(B) from about 0-95, more preferably from about 0.- 70, most preferably from about 0-60 weight percent based on the total weight of the monomers, of at least one vinyl monomer having at least one amide group;

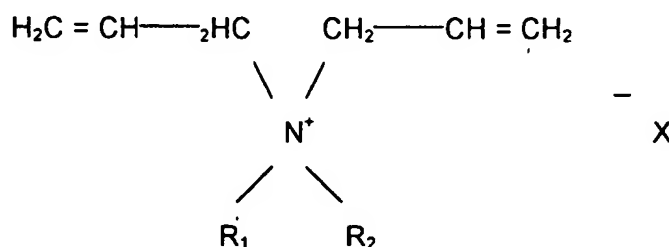


(C) from about 0.5-75, more preferably from about 5-50, most preferably from about 1-50 weight percent based on the total weight of the monomers, of at least one vinyl monomer having a hydrophobic group;

(D) from about 0-10, more preferably from about 0-5 weight percent, based on the total weight of the monomers, of at least one vinyl monomer bearing at least one carboxylic group;

with the proviso that the sum of the percentages of monomers (A) to (D) is 100.

Monomer (A) is preferably of the formula :



in which R<sub>1</sub> and R<sub>2</sub> can be identical or different and is C<sub>1</sub>-C<sub>6</sub> alkyl such as methyl, ethyl, propyl and hexyl. More preferably R<sub>1</sub> is the same as R<sub>2</sub> and is methyl or ethyl. Generally speaking the counter ion (X)<sup>-</sup> of the ammonium atom is any mineral and/or organic anion, such as chloride or sulfate.

The preferred monomers are dimethyldiallylammonium chloride or sulfate and diethyldiallylammonium chloride or sulfate.

Others preferred monomers (A) are selected from the group consisting of: (meth)acryloyloxyethyltrialkylammonium (chloride or methylsulfate), (meth)acryloyloxyhydroxypropyltrialkylammonium (chloride or methylsulfate), (meth)acrylamidopropyltrialkylammonium (chloride or methylsulfate).

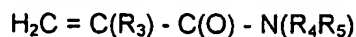
It is also possible to use a precursor of monomer (A). This precursor can be a vinyl monomer having a nitrogen atom which can be subsequently quaternized during or

after the polymerization. These precursors can be selected from vinyl pyridine or vinyl amines such as (meth)acryloyloxyethyltrialkylamine, (meth)acryloyloxyhydroxypropyltrialkylamine modified with glycidyltrialkylammonium chloride, vinyl amides such as (meth)acrylamide including N-substituted analogs thereof  
 5 modified through the Mannich reaction, either pre or post polymerization, which can be subsequently quaternized with methyl chloride, benzyl chloride or dimethyl sulfate, (meth)acrylic acid modified with glycidyltrialkylammonium chloride during pre or post polymerization, vinyl formamide hydrolyzed during pre- or post-polymerization, and the inorganic salt or quaternized derivatives thereof.

10

Other monomers containing amino or quaternary amino groups are disclosed in U.S. Patent 3,766,156, the disclosure of which is incorporated herein by reference.

Examples of monomer (B) are of the formula:



15 in which  $\text{R}_3$  is H or  $\text{C}_1 - \text{C}_6$  alkyl,  $\text{R}_4$  and  $\text{R}_5$ , which can be identical or different are H or  $\text{C}_1 - \text{C}_{12}$  hydrocarbon radical such as alkyl, aryl, alkylaryl or arylalkyl. Examples of alkyl groups are methyl, ethyl, propyl, ethyl-2 hexyl and dodecyl, examples of aryl groups are phenyl and naphthyl, examples of alkyl aryl groups are methylphenyl, ethylphenyl, examples of arylalkyl groups are phenyl methyl and phenylalkyl.

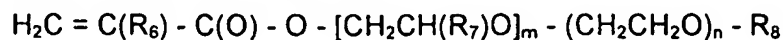
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Examples of suitable monomer (B) are (meth)acrylamide or an alkyl or dialkyl N-substituted (meth)acrylamide and N-(dimethylaminoethyl) acrylamide. It is possible to use a portion of the monomer (B) as a precursor for at least a part of the monomer (A) for example by quaternizing (B), before or after polymerization with a quaternizing agent  
 25 such as methyl chloride as indicated above.

The copolymer also comprises from about 0.5-40 of monomer (C), more preferably, from about 1 - 40, most preferably from about 10 - 30 weight percent of at least one vinyl monomer having a hydrophobic group, based on the total weight of the monomers.

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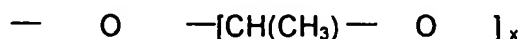
More particularly, monomer (C) can be of the formula:



wherein  $\text{R}_6$  is H or  $\text{C}_1 - \text{C}_6$  alkyl group, preferably H or methyl;  $\text{R}_7$  is  $\text{C}_1 - \text{C}_4$  alkyl, preferably methyl; n is an average number from about 0-100, preferably 0-40 and m is an average

number from about 0-50, preferably 0-10, provided that n is superior or equal to m and the sum of (n + m) is about 0-100; R<sub>8</sub> is a hydrophobic C<sub>8</sub>-C<sub>40</sub> linear or branched alkyl, alkylaryl, or arylalkyl group, preferably a C<sub>18</sub>-C<sub>30</sub> alkyl, more preferably a C<sub>22</sub> behenyl radical or a tristyrylphenyl group of the formula:

5



wherein x is an average number of from about 2 to about 3, and wherein the substituent is randomly distributed around the benzene ring to which it is linked. In embodiments  
10 where the copolymer should include both hydrophobic and hydrophilic groups, the sum of n + m should be greater than one.

The above monomer can be obtained by the reaction of a vinyl monomer of an ester of (meth)acrylic acid with an alkoxyated alcohol or alkoxyated polystyryl phenol or by any  
15 other known process.

Preferred examples of monomer (C) are described in detail in European Patent Nos. EP 011,806 and EP 013,836 and in US Patent Application Serial No. 08/317,261, filed  
20 October 3, 1994. To the extent necessary for completion the disclosures of these references are hereby incorporated herein by reference.

The copolymer can also comprise in some embodiments from 0 to about 10 weight percent of at least one vinyl monomer (D) bearing at least one carboxylic group, more particularly of the formula:

25



in which R<sub>9</sub> is H, C(O)OY or CH<sub>3</sub>, wherein when R<sub>9</sub> is H, R<sub>10</sub> is H, C<sub>1</sub> - C<sub>4</sub> alkyl, or CH<sub>2</sub>COOY; when R<sub>9</sub> is COOY, R<sub>10</sub> is H or CH<sub>2</sub>COOY; or when R<sub>9</sub> is CH<sub>3</sub>, R<sub>10</sub> is H; Y is H or C<sub>1</sub>- C<sub>4</sub> alkyl.

30 Among these monomers, acrylic or methacrylic acid or a mixture thereof with itaconic or fumaric acid are preferred, but crotonic and itaconic acid and half esters of these and other polycarboxylic acids such as maleic acid with C<sub>1</sub> - C<sub>4</sub> alkanols are also suitable, particularly if used in minor amount in combination with acrylic or methacrylic acid. For

most purposes, it is preferable to have at least about 0.5 weight percent and most preferably from about 1 - 5 weight percent of the carboxylic acid monomer.

The copolymer can be a statistical, block or sequenced polymer. Most of the time it is a statistical copolymer.

In a preferred embodiment of the present invention the relative quantity of monomers (A), (B), (C) and optionally (D) are chosen in order to provide a polymer with a molecular weight between about 5,000 and about 5,000,000 more preferably between about 10,000 and about 2,000,000 daltons.

Examples of specific cationic polymers which may be selected include the copolymer of acrylamide, diallyldimethylammonium (chloride or sulfate) and lauryl methacrylate; the copolymer of acrylamide, diallyldimethylammonium (chloride or sulfate), methacrylic acid and the methacrylic ester of tristyrylphenol (having 40 moles of ethylene oxide); the copolymer of acrylamide, (meth)acryloyloxyethyltrialkylammonium (chloride or methylsulfate) and lauryl methacrylate; the copolymer of acrylamide, (meth)acryloyloxyethyltrialkylammonium (chloride or methylsulfate), methacrylic acid and the methacrylic ester of tristyrylphenol (having 40 moles of ethylene oxide); the copolymer of acrylamide, (meth)acryloyloxyhydroxypropyltrialkylammonium (chloride or methylsulfate) and lauryl methacrylate; the copolymer of acrylamide, (meth)acryloyloxyhydroxypropyltrialkylammonium (chloride or methylsulfate), methacrylic acid and the methacrylic ester of tristyrylphenol (having 40 moles of ethylene oxide); the copolymer of acrylamide, (meth)acrylamidopropyltrialkylammonium (chloride or methylsulfate), and lauryl methacrylate; the copolymer of acrylamide, (meth)acrylamidopropyltrialkylammonium (chloride or methylsulfate), methacrylic acid and the methacrylic ester of tristyrylphenol (having 40 moles of ethylene oxide); the copolymer of acrylamide, diethyldiallylammonium (chloride or sulfate), and lauryl methacrylate; and the copolymer of acrylamide, diethyldiallylammonium (chloride or sulfate), methacrylic acid and the methacrylic ester of tristyrylphenol (having 40 moles of ethylene oxide).

When producing copolymers wherein component (C) contains only hydrophobic groups, it is preferred to use a preparation method wherein the hydrophobic monomer or monomers are fed into the polymerization reactor over the course of the polymerization. This feed may be in the form of bulk hydrophobic monomer, or may be in the form of an emulsion of the

hydrophobic monomer system, said emulsion being optionally stabilized with a surface active material or may be in the form of a micellar solution of the hydrophobic monomer system. The emulsion is preferably aqueous, although a solvent which is miscible in water may alternatively be selected. The feed may also contain other components, including water  
5 soluble monomers, chain transfer agents, branching or crosslinking agents, chelants, buffers, polymerization initiators, and similar components known to one skilled in the art as beneficial to the technological application under consideration and the promotion of the intended polymerization. Incorporation of water soluble monomers into the feed along with insoluble monomers provides the ability to control reaction rates that include both fast reacting soluble  
10 as well as fast reacting insoluble monomers.

Water soluble monomers that can be used include various vinyl carboxylic acids (itaconic, malonic, acrylic, methacrylic and others), sulfonic acid monomers such as 2-acrylamidomethylpropanesulfonic acid, various polar monomers such as acrylamide,  
15 methacrylamide, various N- substituted derivatives of these amides, N-vinyl pyrrolidone, N-vinyl formamide, various cationic monomers including diallyldimethylammonium chloride or sulfate, methacrylamidopropyltrimethylammonium chloride, methacryloylethyltrimethylamine and the various alkyl or aryl sulfate or halogen quaternary salts thereof, the acryloyl analog of this family of monomers, and numerous  
20 other water soluble vinyl monomers known to one skilled in the art. Hydrophobic monomers that can be used include styrene, acetoacetoxyethylmethacrylate, vinyl acetate, alkyl, alkylaryl alcohol esters of acrylic or methacrylic acid, butadiene, vinyl chloride, acrylonitrile, 1-vinyl naphthalene, p-methoxystyrene and similar monomers known to one skilled in the art.

25  
Once the monomer system is chosen, a surfactant capable of effectively solubilizing the hydrophobic monomer can be chosen. Various surfactant types may be suitable, chosen from the groups containing anionic, cationic, nonionic, amphoteric and zwitterionic surfactants. The properties of the surfactant may influence the end use effectiveness of  
30 the product, requiring consideration of this factor in surfactant selection as well.

The cationic polymer is typically present in the flotation cell in an amount ranging from about 0.5 to about 5.0 pounds of polymer per ton of pulp to be added to the flotation cell, more preferably from about 1.0 to about 4.0 pounds of polymer per ton of pulp to be added to the

flotation cell, and most preferably from about 1.2 to about 3.5 pounds of polymer per ton of pulp to be added to the flotation cell.

5 The presence of the cationic polymer in the flotation cell can cause an increase in the amount of foam in the flotation cell and also in more fiber being rejected which could otherwise be used. Accordingly, to prevent the problems caused by foaming, a commercially available defoamer may be selected. Examples of defoamers which may be selected include the polypropylene oxide glycol ester of an 18 carbon fatty acid containing colloidal hydrophobic silica. Other defoaming agents which may be selected include mineral oil based  
10 defoamers such as that sold by Rhône-Poulenc under the tradename Fleetcol 9162, ethoxylated castor oil such as those disclosed in U.S. Patent No. 4,871,483, aqueous based defoamers containing emulsified fatty alcohols such as that sold by Rhône-Poulenc under the tradename Colloid 999 and the like. Silicone based defoaming agents are disclosed in U.S. Patent Nos. 4,076,648; 5,380,464 and 5,523,019. To the extent necessary  
15 for completion, the patents referenced in this paragraph and the teachings provided in the patents are hereby expressly incorporated by reference. In practice, when present, the defoamer is present in the flotation cell in amounts ranging from about 0.1 to about 100 microliters per liter of flotation cell.

20 In still other preferred embodiments, the flotation cell can include one or more sources of calcium (2+) ions, magnesium (2+) ions, aluminum (2+) ions or aluminum (3+) ions. Examples of sources of materials which may be selected include the following materials: calcium chloride, aluminum chloride, magnesium chloride, calcium sulfate, magnesium sulfate or aluminum sulfate. In practice, when present, the source of positive ions is present  
25 in the flotation cell in amounts ranging from about 10 to about 1000 ppm, more preferably between about 300 and about 500 ppm.

Optionally present in the flotation cell is one or more nonionic surfactants as defined above with respect to the pulping step. The amount of nonionic surfactant present is that which  
30 yields the same percentages as that present in the pulping step (i.e., between about 0.05 to about 3.0 percent by weight of the paper added to the pulper). Often it is not necessary to add additional nonionic surfactant as that which is present in the slurry produced in the pulper is sufficient for functioning in the flotation cell, although additional nonionic surfactant may be added.

Also optionally present in the flotation cell is one or more anionic polyelectrolytes. The amount of anionic polyelectrolyte present is that which yields the same percentages as that present in the pulping step (i.e., about 0.01 to about 2.0 percent by weight of the dry weight of all paper stock). The polyelectrolyte may, as a matter of fact, be identical to that which is present as the binder to the hydrophilic ink. Often it is not necessary to add additional polyelectrolyte as that which is present in the slurry produced in the pulper is sufficient for functioning in the flotation cell, although additional anionic polyelectrolyte may be added.

10

Other materials which may be added to the flotation cell, which are considered optional, include pH adjusting chemicals, bleaches, chelants, clarification aids and mixtures thereof.

The slurry is maintained in the flotation cell for a time, temperature and rate of agitation necessary to produce a foam which contains a significant amount of the removed ink. Such process conditions typically comprise treating the slurry at about 40°C to about 50°C for about 1 to about 30 minutes, injecting air into the cell in an amount sufficient to disperse air bubbles throughout the mixture, with good agitation and without becoming so turbulent as to dislodge ink from the air bubbles or increase the degree of ink dispersion. This amount of injection is typically about 1 cell volume of air per minute. The concentration of the paper fibers is about 0.5 to about 2.0% of the cell.

Once flotation has been completed, the foam which forms above the slurry in the flotation is removed by methods known in the art such as by a scraper. From the remaining slurry, paper can be produced which has a high level of brightness.

Alternatively, the remaining slurry may be subjected to additional processing steps such as post flotation wash procedures as would be recognized by those skilled in the art to yield even more superior paper products.

30

The invention is described in greater detail by the following non-limiting examples.

#### Example 1

A mixed recycle furnish is prepared comprising 30% magazine (MacWeek), 40% letterpress (New York Times) and 30% flexographic news (Knoxville News-Sentinel). Average age of the furnish is 3 months. The publications are cut into 0.5 cm wide strips in an office shredder; the magazine is pre-pulped in a Waring blender for 2 minutes at 3.5% consistency and then added along with the newsprints to a Kitchen Aid blender. This admixture is pulped 5 minutes at 10% consistency in the presence of 0.2% surfactant (InkMaster® 750 (Rhône-Poulenc Inc.)) based on oven dry fiber (ODF), sodium hydroxide, sodium silicate (3% Type N based on ODF) and hydrogen peroxide (0.5% based on ODF).

10

Pulper pH is adjusted to 9.5 using sodium hydroxide. Pulper temperature is controlled at 50°C. This pulp is diluted to 1.2% consistency, and added along with flotation aids to a Denver cell. This is gently mixed with a 3 cm. diameter marine propeller for 3 minutes at 120 rpm. Flotation is conducted with a Denver D1 induced air mixer at 1600 RPM for 3 minutes in a 1 liter glass cell. Foam is manually scraped from the top of the float cell. Flotation pH is 9.0 and the temperature is maintained at 50°C.

15

A brightness pad is prepared by filtering 300 ml of float cell accepts through a very coarse filter paper (VWR grade 417). Filter paper is stripped from the pad. The pad is pressed at 45 psig, then air dried overnight. The brightness pads are cut into 7 equal wedge-shaped segments, then stacked. Brightness measurements of each segment, both top and bottom, are taken using a Technidyne Handi-Brite while stacked. The float cell filtrate turbidity is measured using a Hach Laser Zee turbidimeter. Float cell rejects are weighed, filtered and dried.

25

The performance of a series of experimental cationic polymers as flotation additives is investigated under the previously outlined laboratory deinking conditions. Two inventive cationic polymers, a copolymer of acrylamide, diallyldimethylammonium chloride and lauryl methacrylate having an approximate 30-68-2 mole ratio (referred to as DV-A) and a copolymer of acrylamide, diallyldimethylammonium chloride, methacrylic acid and the methacrylic ester of tristyrylphenol having 40 moles of ethylene oxide in an approximate 30-68-.5-1.5 mole ratio (referred to as DV-B), a conventional polyamine cationic coagulant, Magnifloc 634C sold by Cytec (referred to as PC) and flotation with no additional polymer are tested. The cationic polymer is added into the flotation cell at a dosage of about 4 lb./dry ton of pulp. Results for this set of tests are shown in Table 1.

35



The inventive cationic copolymers, particularly DV-A, are produced from a two solution feed, the first including a free radical polymerization initiator such as ammonium persulfate and the other being a monomer solution containing both a hydrophilic and a hydrophobic monomer. For example, a reactor charge is prepared by forming a solution of 77.58 parts of 62% diallyldimethylammonium chloride, 102.4 parts deionized water, 0.096 parts of ammonium persulfate, 0.02 parts of a 40% solution of pentasodium diethylenetriamine pentaacetic acid and 20 parts of sodium lauryl sulfate. An initiator feed solution is added to the reactor with 50 parts of deionized water and 1.152 parts of ammonium sulfate. A monomer solution is separately added to the reactor which contains 3.25 parts lauryl methacrylate, 91.69 parts acrylamide, 124 parts deionized water and 31 grams of sodium lauryl sulfate. The above solution is homogenized for four minutes. After polymerization a white viscous polymer solution is obtained. This solution is considered to be the DV-A cationic polymer. The DV-B cationic polymer is similarly prepared.

Additional experiments are conducted by the addition of calcium ions (+2) to the flotation cell which includes the DV-A polymer. Three experiments are conducted using  $\text{Ca}^{2+}$  levels of 0, 88 ppm and 175 ppm. The presence of  $\text{Ca}^{2+}$  ions exhibit a strong positive effect in assisting the action of polymer DV-A to reduce float accept water turbidity. This data is demonstrated in Figure 1.

Further experiments are conducted by the addition of surfactant or surfactant/defoamer blends to the flotation cells. The surfactant selected is an EO-PO C-16-C20 fatty alcohol (InkMaster® 750, Rhône-Poulenc Inc., referred to as SDA) and is added at a level of 4 lb/dry ton and the defoamer added is a polypropylene oxide glycol ester of a C18 fatty acid containing hydrophobic silica (Colloid 999 - Rhône-Poulenc) which is added at a level of 10 microliters per liter of flotation cell. The data and results of these experiments are shown in Table 2.

#### Example 2

A series of 6 flotation runs are conducted using a process sequence of high consistency pulping, detrashing, fine screen cleaning, four passes through a 75 gpm pressurized flotation cell, followed by forward cleaning, pressing and washing. The furnish used is

30% flexographic newsprint, 30% magazine and 40% conventional newsprint. Pulping consistency is targeted at 15%, however equipment limitations generally require addition of water to about 12% consistency. Nonionic surfactant (0.2% ODF), sodium hydroxide, sodium silicate (3% Type N ODF) and hydrogen peroxide (0.5% ODF) are used in the pulper. The chemicals used in the pulper are identical to those disclosed in Example 1. Pulping is performed using a Tridyne® impeller at about 50 RPM for 20 minutes. Pulper pH is adjusted to 9.5 using sodium hydroxide. Pulping temperature is controlled at 50°C. Consistency, freeness, filter pad brightness, dirt measurements (total particle, visible dirt, and TAPPI dirt), float accept filtrate turbidity, and fiber length distribution (Kajaani) measurements are obtained at various points in the process.

Additional experiments on the effects of agitation on accept filtrate turbidity on float feeds are conducted by timed mixing of the float feed using a magnetic stirrer. Cationic polymers and other flotation chemicals are added to the float feed chest and mixed for 3 minutes. Normal practice is to mix the float feed chest during the entire flotation run to prevent fiber segregation, however these mixers are turned off in order to maximize the turbidity reduction effects of the additives employed in these experiments.

The pulper additives and flotation additives for the six different runs are shown in Tables 3 and 4. The dispersant is the copolymer of maleic anhydride and isobutylene.

Figure 2 shows the effects of polymer addition on filtered float accept turbidity. Under the conditions of this series of experiments, the use of cationic polymer is successful in reducing float accept turbidity from about 2000 NTU to levels as low as 30 NTU.

Figure 3 shows a comparison between polymer dose relationships in the cells, mixing of the float cell feed using magnetic mixers for fixed time periods followed by filtration of the feed and turbidity measurement.

Figure 4 shows the effect of polymer addition on the visible dirt content of sheets made from the flotation feed. There is a general trend of increasing visible dirt vs. polymer dose level.

Figure 5 shows similar data for post-flotation cleaner accepts.

Figure 6 shows the total dirt particle counts for flotation feed and Figure 7 shows the cleaner accepts. These figures demonstrate the effects of the cationic polymer on ink particle sizes. Process brightness gains are where differences in polymer structure are the most evident.

Figures 8, 9 and 10 demonstrate that the float feed brightness, final brightness, and total process brightness gains consistently show the effect of polymer dose and type on fiber brightness.

Figure 11 shows the float accept brightness results. According to the Figure, the brightness actually increases with increasing polymer dose. This is believed to be due to a yield/brightness effect; that is the overall brightness increases as yield losses increase with increasing polymer. This trend reverses after a wash step.

Figure 12 shows fiber length variations with the process as measured using Kajaani methodology. The flotation process appears to remove fines but does not seem to affect the fiber length.

Having described the invention in detail and by reference to the preferred embodiments thereof, it will be apparent that modifications and variations are possible without departing from the scope of the appended claims.

## WHAT IS CLAIMED IS:

1. A process for removing water borne flexographic inks from paper stock comprising the steps of:

5

(a) forming a slurry by pulping paper containing water borne flexographic inks in an aqueous medium having a pH of greater than 6 which includes:

10

- (1) one or more pH adjusting agents;
- (2) one or more nonionic surfactants; and
- (3) one or more anionic polyelectrolytes; and

(b) subjecting the slurry produced in step (a) to a flotation cell including one or more cationic polymers.

15

2. The process according to claim 1 wherein the pH of said aqueous medium of step (a) is between about 6 to about 10.5.

3. The process according to claim 2 wherein the pH of said aqueous medium of step (a) is between about 9 to about 10.

20

4. The process according to claim 3 wherein the pH of said aqueous medium of step (a) is between about 9 to about 9.5.

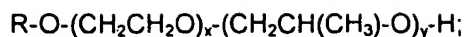
5. The process according to claim 1 wherein said pH adjusting agent of said aqueous medium of step (a) is selected from the group consisting of NaOH, NH<sub>4</sub>OH, KOH, Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, HCl, CH<sub>3</sub>COOH and mixtures thereof.

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6. The process according to claim 1 wherein said nonionic surfactant of said aqueous medium of step (a) is selected from the group consisting of

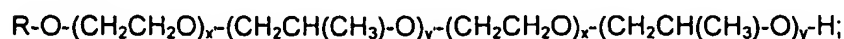
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- a) a fatty alcohol having a carbon number of from about 8 to about 22 alkoxylated with ethylene oxide and propylene oxide, as defined by the formula



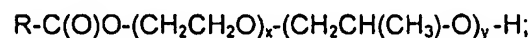
wherein R is a straight-chain or branched alkyl group having a carbon number of from about 8 to about 22, x represents the number of oxyethylene groups per molecule and is in the range of from about 3 to about 25, and y represents the number of oxypropylene groups per molecule and is in the range of from about 2 to about 10;

- b) a fatty alcohol having a carbon number of from about 8 to about 22 alkoxylated with ethylene oxide and propylene oxide, as defined by the formula:



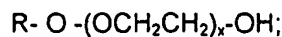
wherein R is a straight-chain or branched alkyl group having a carbon number of from about 8 to about 22, x and x' may be the same or different and represents the number of oxyethylene groups per molecule and is in the range of from about 2 to about 25, and y and y' may be the same or different and represents the number of oxypropylene groups per molecule and is in the range of from 0 to about 10;

- c) a fatty acid having a carbon number of from about 8 to about 22 alkoxylated with ethylene oxide and propylene oxide, as defined by the formula:



wherein R is a straight-chain or branched alkyl group having a carbon number of from about 8 to about 22, x represents the number of oxyethylene groups per molecule and is in the range of from about 3 to about 25, and y represents the number of oxypropylene groups per molecule and is in the range of from about 2 to about 15;

- d) an aromatic alcohol having alkyl chain(s) with a carbon number of from about 8 to about 20 alkoxylated with ethylene oxide, as defined by the formula:

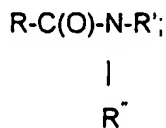


R'

wherein R and R' is H or an alkyl group and the alkyl is branched or straight-chain having a carbon number of from about 8 to about 14, x is

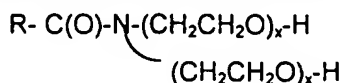
the number of oxyethylene groups per molecule and is in the range of from about 1 to about 20;

e) a fatty amide of alkanolamide of the formula:



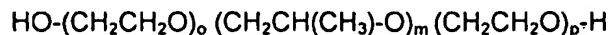
wherein R' and R'' are H or CH<sub>2</sub>CH<sub>2</sub>OH or CH<sub>2</sub>CH(CH<sub>3</sub>)-OH and R is a fatty alkyl group having a carbon number of from about 8 to about 20;

f) an alkoxyated fatty acid amide of alkanolamide of the formula:



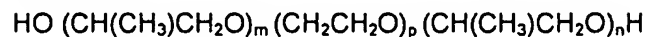
wherein R is a fatty alkyl group having a carbon number of from about 8 to about 20, and x represents the number of oxyethylene groups per molecule and is in the range of from about 2 to about 10;

g) a propylene glycol alkoxylate of the formula:



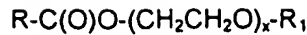
wherein o and p are the number of oxyethylene groups per molecule and are in the range of from about 3 to about 15 and m is number of oxypropylene groups per molecule and is in the range of from about 25 to about 40;

h) a block or random copolymer of ethylene and propylene oxide of the formula:



wherein m and n are the number of oxypropylene groups per molecule and are in the range of from about 10 to about 25 and p is the number of oxyethylene groups per molecule and is in the range of from about 5 to about 25;

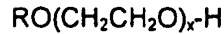
i) an ethoxylated fatty acid, glycol or polyethylene glycol ester of the formula:



wherein R is a fatty alcohol greater than C<sub>8</sub>, R<sub>1</sub> is an alkyl of greater than C<sub>8</sub> or H, and x represents the number of oxyethylene groups per molecule and is in the range of from about 5 to about 200; and

5

- j) an ethoxylated fatty alcohol of the formula:



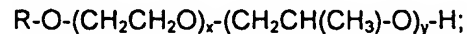
wherein R is a fatty alcohol and x represents the number of oxyethylene groups per molecule and is in the range of from about 1 to about 20.

10

7. The process according to claim 6 wherein said nonionic surfactant of said aqueous medium of step (a) is selected from the group consisting of

- a) a fatty alcohol having a carbon number of from about 8 to about 22 alkoxylated with ethylene oxide and propylene oxide, as defined by the formula

15

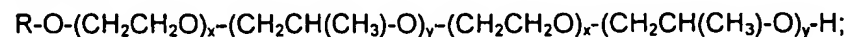


wherein R is a straight-chain or branched alkyl group having a carbon number of from about 8 to about 22, x represents the number of oxyethylene groups per molecule and is in the range of from about 3 to about 25, and y represents the number of oxypropylene groups per molecule and is in the range of from about 2 to about 10;

20

- b) a fatty alcohol having a carbon number of from about 8 to about 22 alkoxylated with ethylene oxide and propylene oxide, as defined by the formula:

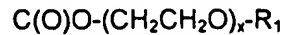
25



wherein R is a straight-chain or branched alkyl group having a carbon number of from about 8 to about 22, x and x' may be the same or different and represents the number of oxyethylene groups per molecule and is in the range of from about 2 to about 25, and y and y' may be the same or different and represents the number of oxypropylene groups per molecule and is in the range of from 0 to about 10; and

30

- c) an ethoxylated fatty acid, glycol or polyethylene glycol ester of the formula:



- 5 wherein R is a fatty alcohol greater than  $\text{C}_8$ ,  $\text{R}_1$  is an alkyl of greater than  $\text{C}_8$  or H, and x represents the number of oxyethylene groups per molecule and is in the range of from about 5 to about 200.

8. The process according to claim 6 wherein said nonionic surfactant is present in step (a) in an amount of about 0.05 to about 1.0 percent by weight of the dry weight of all paper stock in step (a).  
10

9. The process according to claim 1 wherein said one or more anionic polyelectrolytes in step (a) is selected from the group consisting of copolymers of maleic anhydride and isobutylene, polyacrylic acid and its acid salts, the formaldehyde condensate of  
15 methylnaphthalene sulfonic acid, polymers containing 2-acrylamidopropane sulfonic acid, methacrylic acid, itaconic acid, vinylic compounds with anionic functional groups, condensation polymers containing anionic functional groups, naturally occurring polymers containing anionic functionality and mixtures thereof.

- 20 10. The process according to claim 9 wherein said one or more anionic polyelectrolytes in step (a) is a copolymer of maleic anhydride and isobutylene.

11. The process according to claim 6 wherein said anionic polyelectrolyte is present in step (a) in an amount of about 0.01 to about 2.0 percent by weight of the dry weight of  
25 all paper stock in step (a).

- 12 The process according to claim 1 wherein the pH of said aqueous medium of step (b) is between about 6 to about 10.5.

- 30 13 The process according to claim 12 wherein the pH of said aqueous medium of step (b) is between about 8.5 to about 9.5.

- 14 The process according to claim 13 wherein the pH of said aqueous medium of step (b) is between about 9 to about 9.5.



15. The process according to claim 1 wherein said cationic polymer of step (b) is a copolymer of:

5 (A) from about 0.1 - 99.5 weight percent based on total weight monomers of at least one vinyl monomer having at least one quaternized nitrogen atom;

(B) from about 0 - 95, weight percent based on the total weight of the monomers, of at least one vinyl monomer having at least one amide group;

10

(C) from about 0.5-75, weight percent based on the total weight of the monomers, of at least one vinyl monomer containing a hydrophobic group, and

(D) from about 0 -10 weight percent, based on the total weight of the monomers, of at least one vinyl monomer bearing at least one carboxylic group;

15

with the proviso that the sum of the percentages of monomers (A) to (D) is 100.

16. The process according to claim 1 wherein said flotation cell further comprises a source of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{2+}$  or  $\text{Al}^{3+}$  ions.

20

17. The process according to claim 1 wherein said flotation cell further comprises a defoaming agent.

25 18. A process for removing flexographic inks from substrates comprising the steps of:

(a) pulping said substrates to form a slurry; and

(b) subjecting said slurry to a flotation cell including one or more cationic polymers, a source of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{2+}$  or  $\text{Al}^{3+}$  ions and a defoaming agent.

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FIG. 1

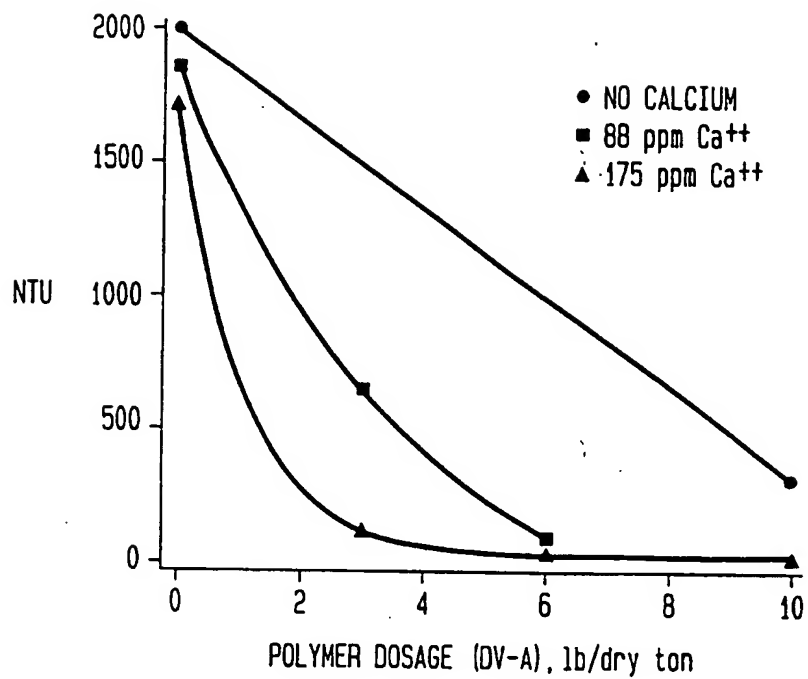
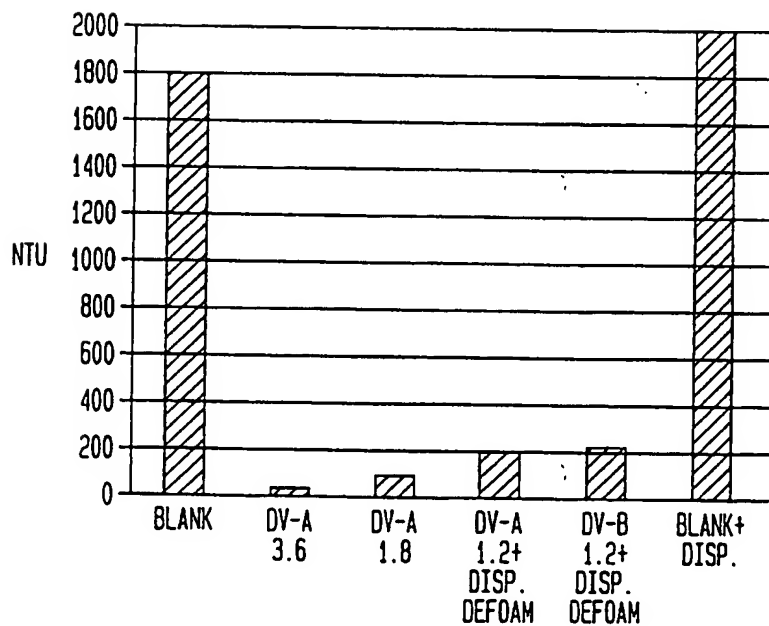


FIG. 2



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FIG. 3

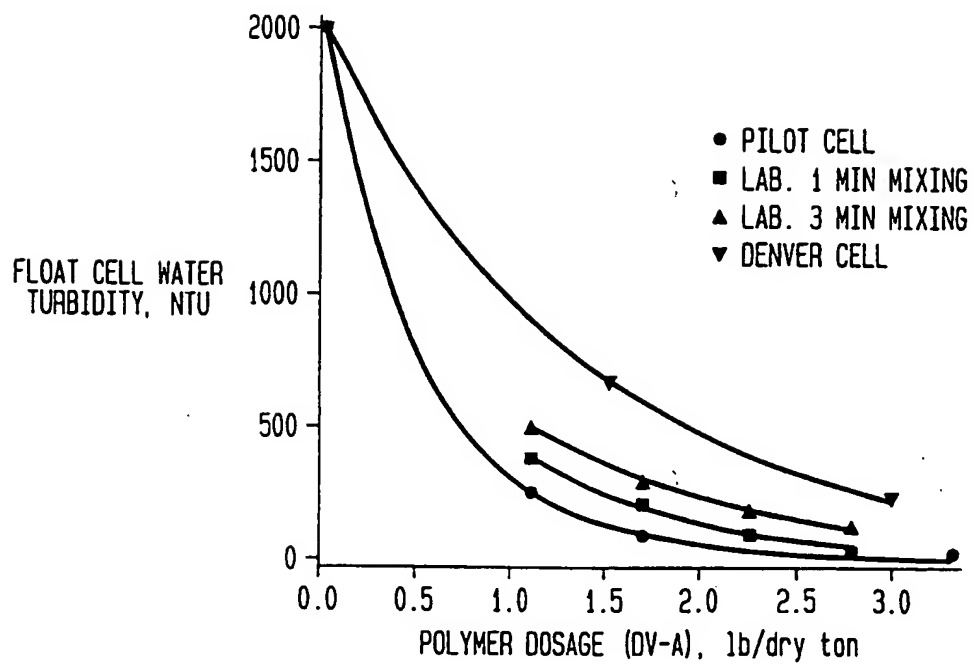
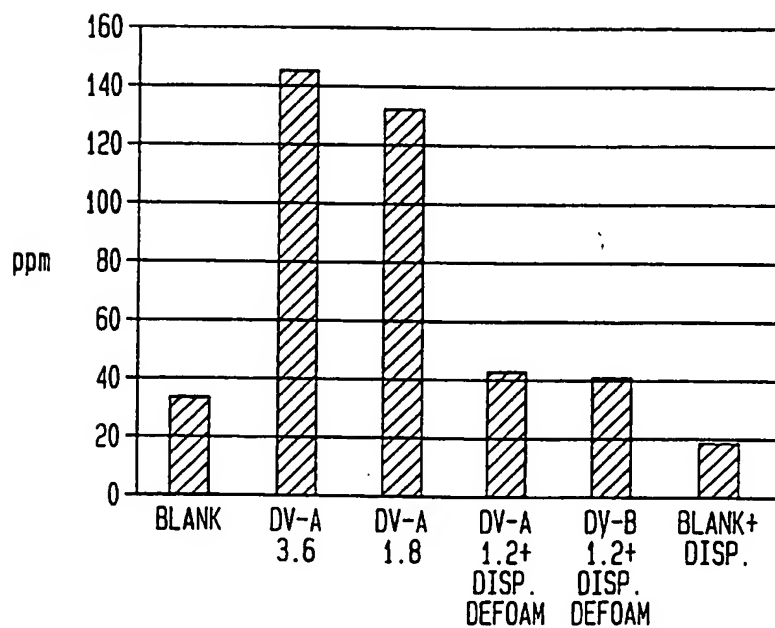


FIG. 4



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FIG. 5

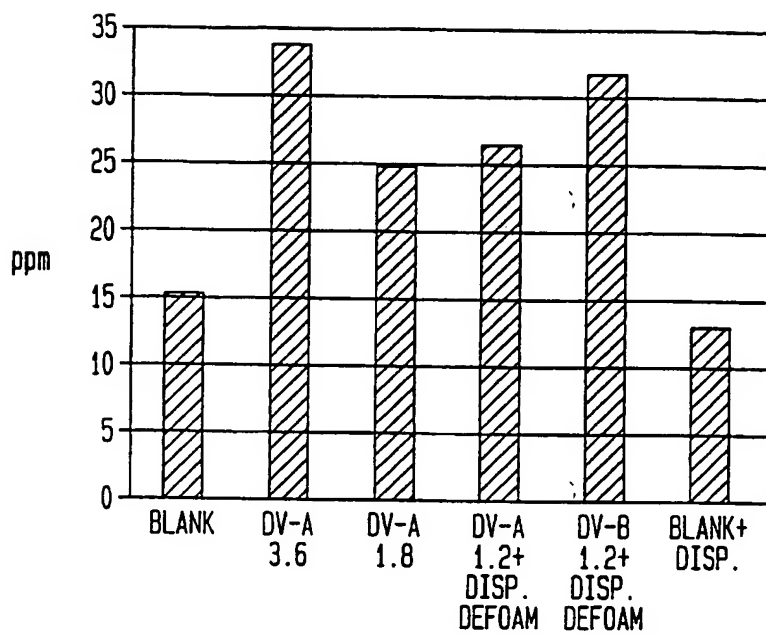
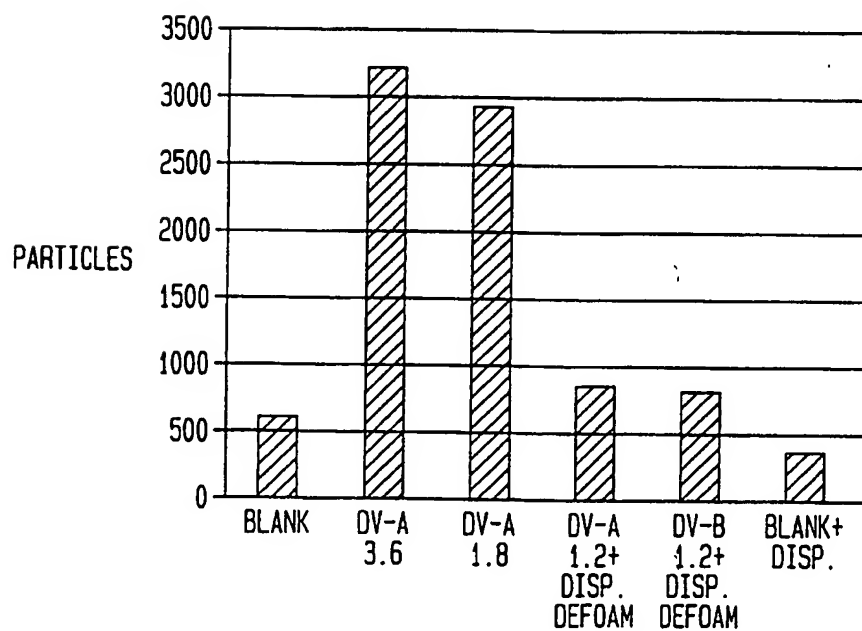


FIG. 6



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FIG. 7

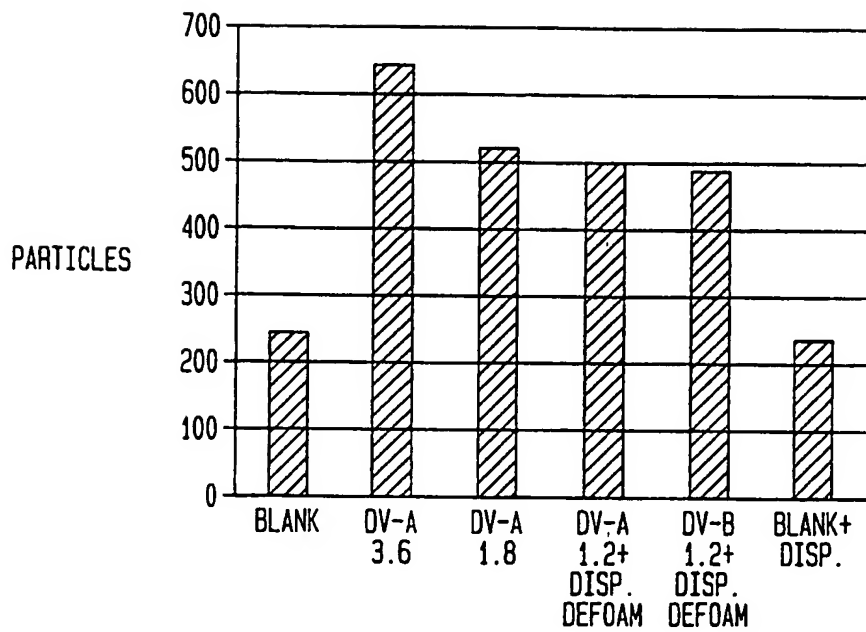
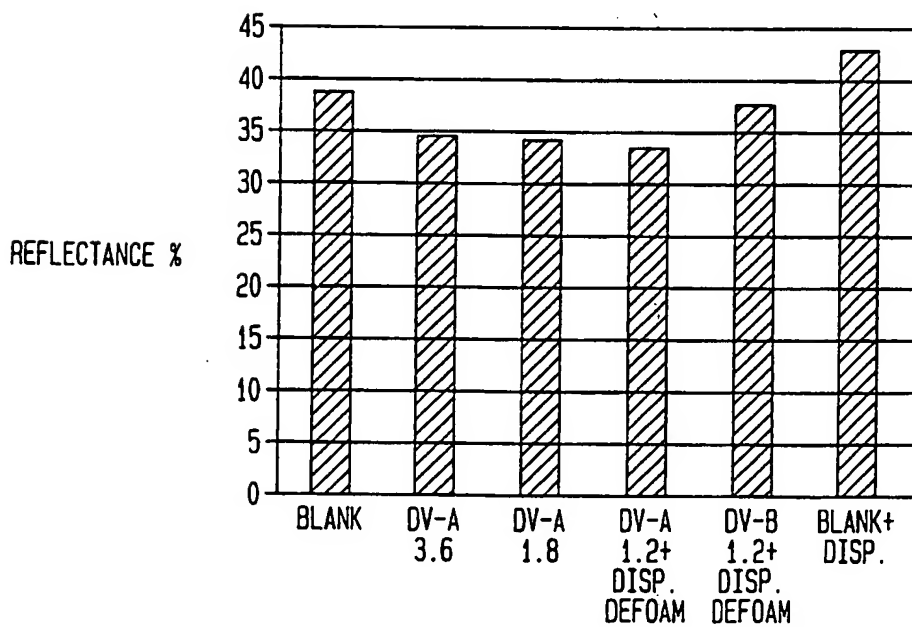


FIG. 8



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FIG. 9

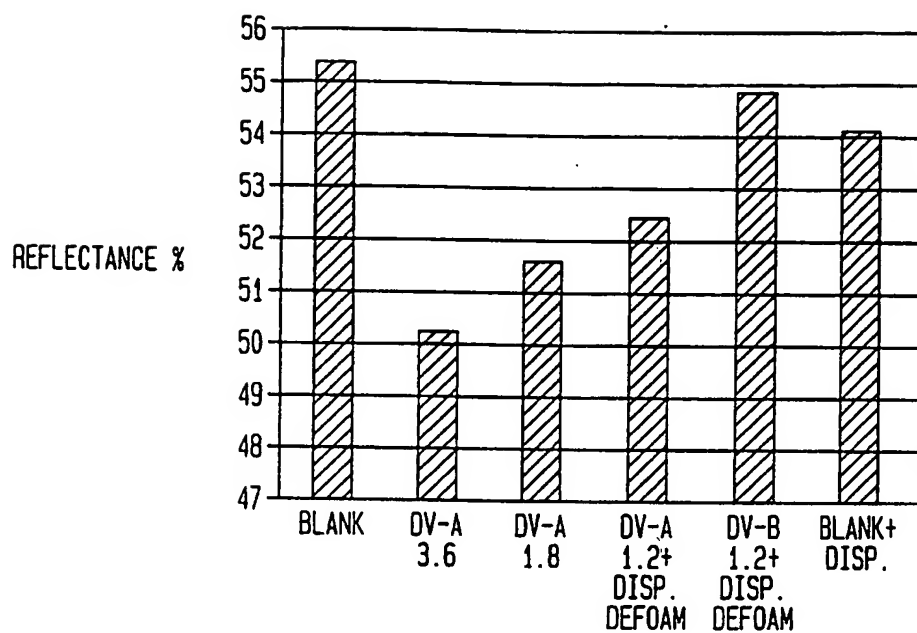
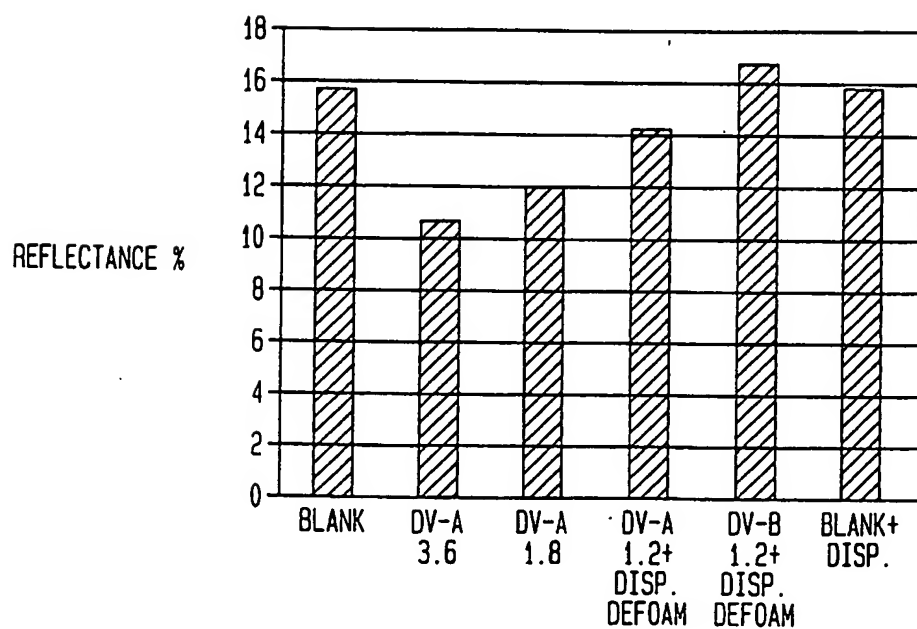


FIG. 10



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FIG. 11

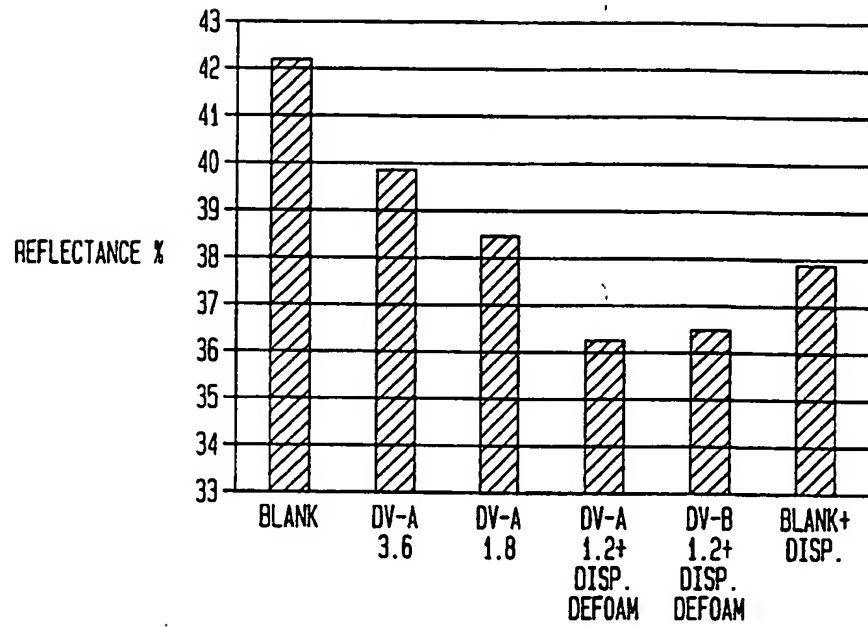
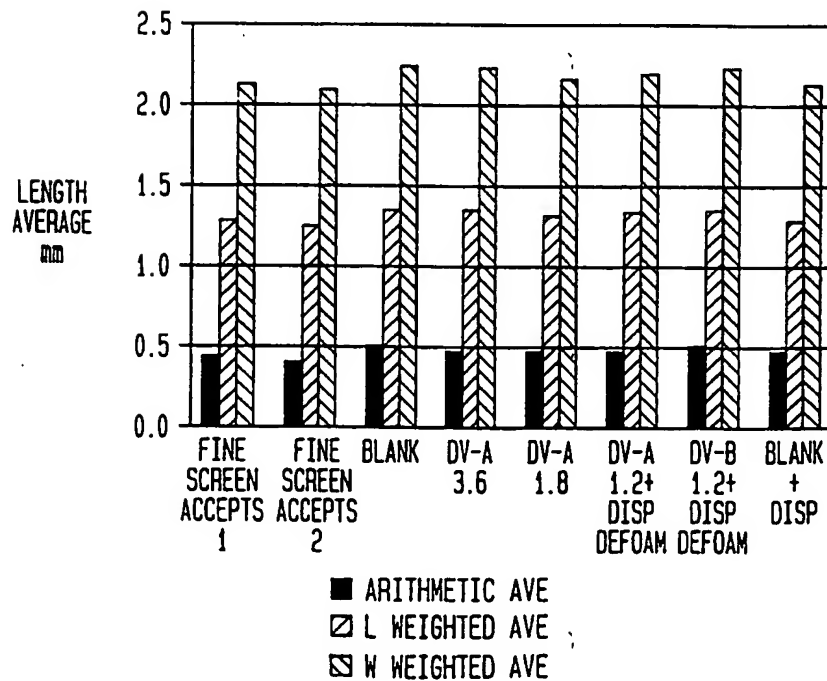


FIG. 12



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TABLE 1: POLYMER COMPARISON

POLYMER	NTU	REFLECTANCE (%)	REJECT VOLUME	FIBER YIELD
DV-B	260	51.0	290	0.63
DV-A	244	49.8	255	0.66
PC	426	50.7	344	0.60
NONE	2000+	48.8	120	0.81

TABLE 2: SURFACTANT AND DEFOAMER YIELD EFFECTS

SURFACTANT	POLYMER	NTU	REFLECTANCE (%)	REJECT VOLUME	FIBER YIELD
SDA	NONE	1644	45.63	107.1	0.84
SDA	DV-B	241	48.47	265.4	0.67
SDA/D-1	DV-B	207	45.33	116.9	0.85

TABLE 3: PULPER ADDITIVES. OOF

PULP	FLOAT	SDA	DISPERSANT	SILICATE TYPE N	H <sub>2</sub> O <sub>2</sub> (100%)
1	1	0.20%		3%	0.50%
1	2	0.20%		3%	0.50%
1	3	0.20%		3%	0.50%
2	4	0.20%	0.20%	3%	0.50%
2	5	0.20%	0.20%	3%	0.50%
2	6	0.20%	0.20%	3%	0.50%

TABLE 4: FLOAT FEED ADDITIVES

PULP	FLOAT	DEFOAMER D-1	POLYMER TYPE	POLYMER lb/ton	Ca <sup>++</sup> ppm
1	1	-	-	-	-
1	2	-	DV-A	3.33	175
1	3	-	DV-A	1.67	175
2	4	10 ppm	DV-A	1.2	175
2	5	10 ppm	DV-B	1.2	175
2	6	-	-	1.2	-



# INTERNATIONAL SEARCH REPORT

national Application No

PCT/US 98/07250

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 D21C5/02

According to International Patent Classification(IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	US 5 632 857 A (LARSON ERIC H) 27 May 1997 see column 2, line 55 - column 9, line 21	1-14
P,Y	see the whole document	1-10, 12-14
Y	US 5 415 733 A (ROBINSON PETER M ET AL) 16 May 1995 see the whole document	1,6-8, 15,16,18
Y	DE 40 07 596 A (HENKEL KGAA) 12 September 1991 see page 2, line 3 - page 4, line 58	1,6-8
Y	WO 96 31646 A (KAO CORP ;IRINATSU YUICHI (JP); MIYAUCHI YOSHITAKA (JP); TAKAHASHI) 10 October 1996 see the whole document	1-8, 12-16,18
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

1 July 1998

Date of mailing of the international search report

10/07/1998

Name and mailing address of the ISA  
European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

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Nestby, K

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International Application No  
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>DATABASE WPI Section Ch, Week 7913 Derwent Publications Ltd., London, GB; Class A97, AN 79-24833B XP002007473 &amp; JP 54 023 705 A (HONSHU PAPER MFG CO LTD) see abstract ---</p>	1,16,18
Y	<p>US 4 599 190 A (MALONEY JAMES E ET AL) 8 July 1986 see the whole document ---</p>	1,6-10
A	<p>US 5 094 716 A (LETSCHER MARY B) 10 March 1992 see column 4, paragraph 2 ---</p>	17,18
A	<p>US 5 384 010 A (HOU MEAN-JENG ET AL) 24 January 1995 ---</p>	
A	<p>US 5 449 725 A (KANLUEN RATANA ET AL) 12 September 1995 -----</p>	

# INTERNATIONAL SEARCH REPORT

Information on patent family members

national Application No

PCT/US 98/07250

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5632857	A	27-05-1997	NONE	
US 5415733	A	16-05-1995	CA 2163513 A	08-12-1994
			EP 0702734 A	27-03-1996
			FI 955714 A	27-11-1995
			JP 8511065 T	19-11-1996
			NO 954744 A	23-11-1995
			WO 9428237 A	08-12-1994
DE 4007596	A	12-09-1991	AU 7455191 A	10-10-1991
			WO 9113859 A	19-09-1991
WO 9631646	A	10-10-1996	CA 2213823 A	10-10-1996
			EP 0819190 A	21-01-1998
			JP 8337984 A	24-12-1996
			JP 8337985 A	24-12-1996
			JP 8337986 A	24-12-1996
US 4599190	A	08-07-1986	US 4810328 A	07-03-1989
			BR 8007390 A	26-05-1981
			CA 1151812 A	16-08-1983
			FI 803553 A,B,	14-05-1981
			GB 2063326 A,B	03-06-1981
			SE 456250 B	19-09-1988
			SE 8007949 A	14-05-1981
			SE 456251 B	19-09-1988
			SE 8601383 A	25-03-1986
			SE 456252 B	19-09-1988
			SE 8601384 A	25-03-1986
			SE 456253 B	19-09-1988
			SE 8601385 A	25-03-1986
			US 4518459 A	21-05-1985
			US 4643800 A	17-02-1987
US 5094716	A	10-03-1992	AU 653355 B	29-09-1994
			AU 8254991 A	26-03-1992
			CA 2026055 A	20-03-1992
			US 5387355 A	07-02-1995
			US 5281348 A	25-01-1994

# INTERNATIONAL SEARCH REPORT

Information on patent family members

national Application No

PCT/US 98/07250

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5384010 A	24-01-1995	CA 2130941 A	28-02-1995
US 5449725 A	12-09-1995	CA 1339231 A	05-08-1997
		DE 69025350 D	28-03-1996
		DE 69025350 T	27-06-1996
		EP 0394690 A	31-10-1990
		JP 2284969 A	22-11-1990
		JP 2611026 B	21-05-1997
		JP 2683232 B	26-11-1997
		JP 9176978 A	08-07-1997